

## Environmental Protection Agency

## Pt. 60, App. A-5, Meth. 15A

12.5 Concentration of Generated Recovery Gas.

$$C_{RG} = \frac{(C_{cos})(Q_{cos})}{Q_{cos} + Q_{N_2}} \quad \text{Eq. 15A-4}$$

12.6 Recovery Efficiency for the System Performance Check.

$$R = \frac{C_{RG(m)}}{C_{RG(act)}} \times 100 \quad \text{Eq. 15A-5}$$

### 13.0 Method Performance

13.1 Analytical Range. The lower detectable limit is 0.1 ppmv when sampling at 2 lpm for 3 hours or 0.3 ppmv when sampling at 2 lpm for 1 hour. The upper concentration limit of the method exceeds concentrations of reduced sulfur compounds generally encountered in sulfur recovery plants.

13.2 Precision. Relative standard deviations of 2.8 and 6.9 percent have been obtained when sampling a stream with a reduced sulfur compound concentration of 41 ppmv as SO<sub>2</sub> for 1 and 3 hours, respectively.

13.3 Bias. No analytical bias has been identified. However, results obtained with this method are likely to contain a positive bias relative to emission regulations due to the presence of nonregulated sulfur compounds (that are present in petroleum) in the

emissions. The magnitude of this bias varies accordingly, and has not been quantified.

### 14.0 Pollution Prevention. [Reserved]

### 15.0 Waste Management. [Reserved]

### 16.0 References

1. American Society for Testing and Materials Annual Book of ASTM Standards. Part 31: Water, Atmospheric Analysis. Philadelphia, Pennsylvania. 1974. pp. 40-42.
2. Blosser, R.O., H.S. Oglesby, and A.K. Jain. A Study of Alternate SO<sub>2</sub> Scrubber Designs Used for TRS Monitoring. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York. Special Report 77-05. July 1977.
3. Curtis, F., and G.D. McAlister. Development and Evaluation of an Oxidation/Method 6 TRS Emission Sampling Procedure. Emission Measurement Branch, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. February 1980.
4. Gellman, I. A Laboratory and Field Study of Reduced Sulfur Sampling and Monitoring Systems. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York. Atmospheric Quality Improvement Technical Bulletin No. 81. October 1975.
5. Margeson, J.H., et al. A Manual Method for TRS Determination. Journal of Air Pollution Control Association. 35:1280-1286. December 1985.

## 17.0 Tables, Diagrams, Flowcharts, and Validation Data

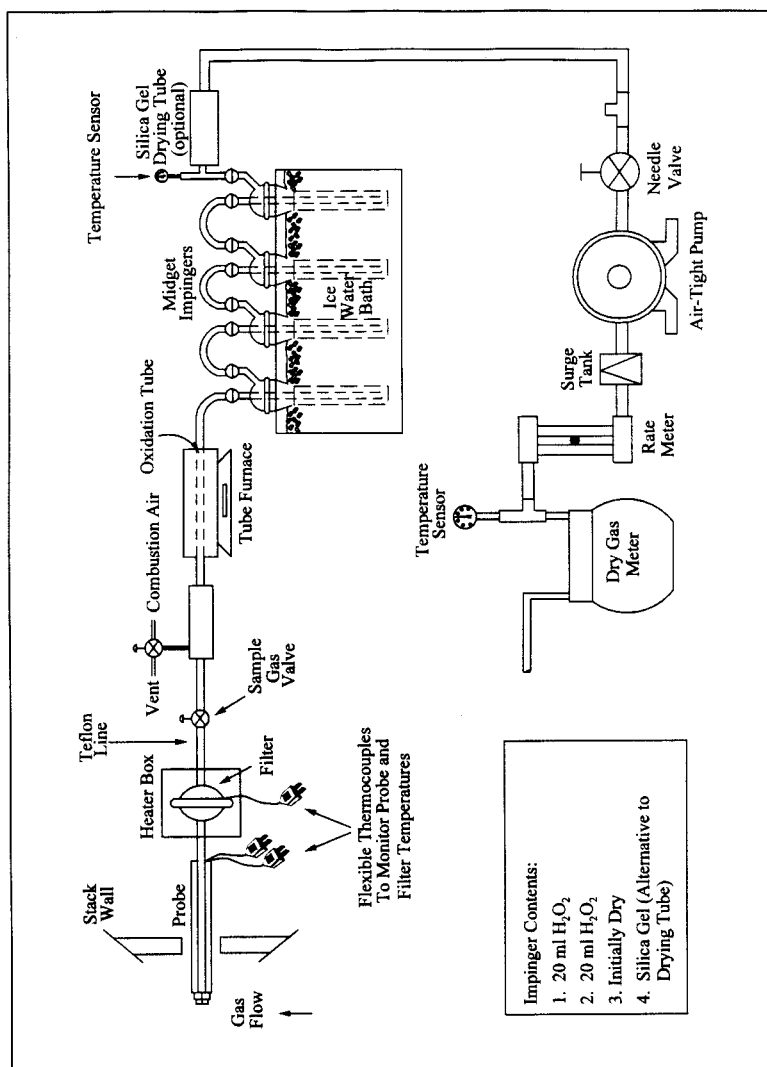


Figure 15A-1. Method 15A Sampling Train.

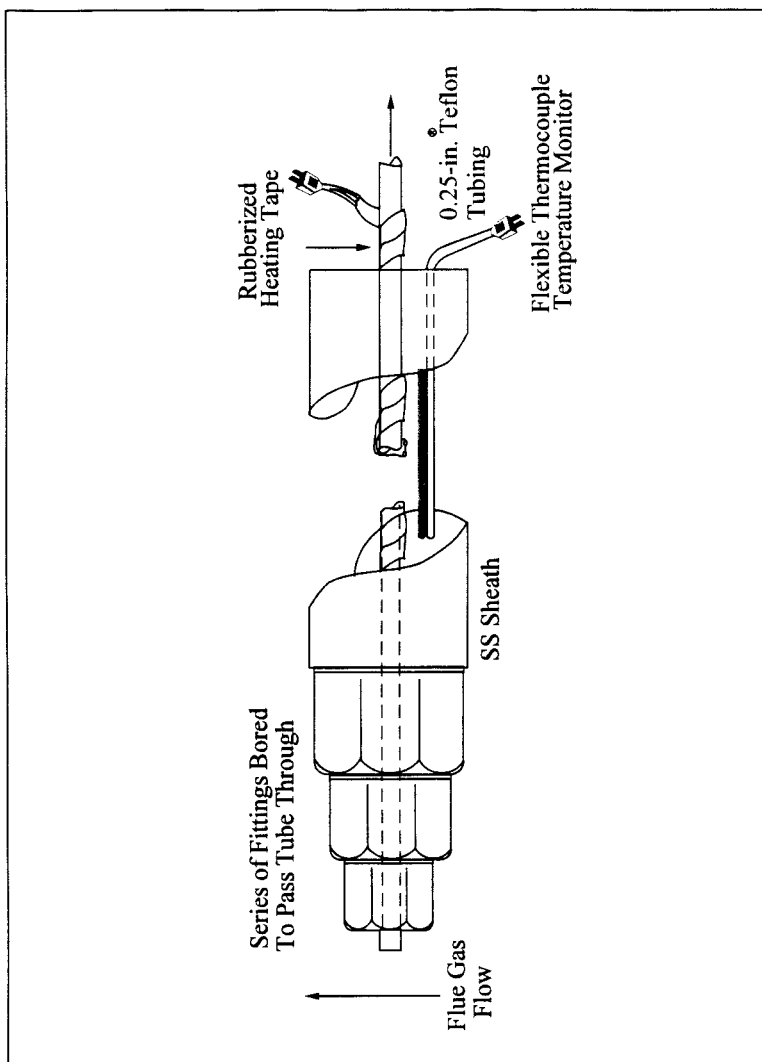


Figure 15A-2. Method 15A Sampling Probe.

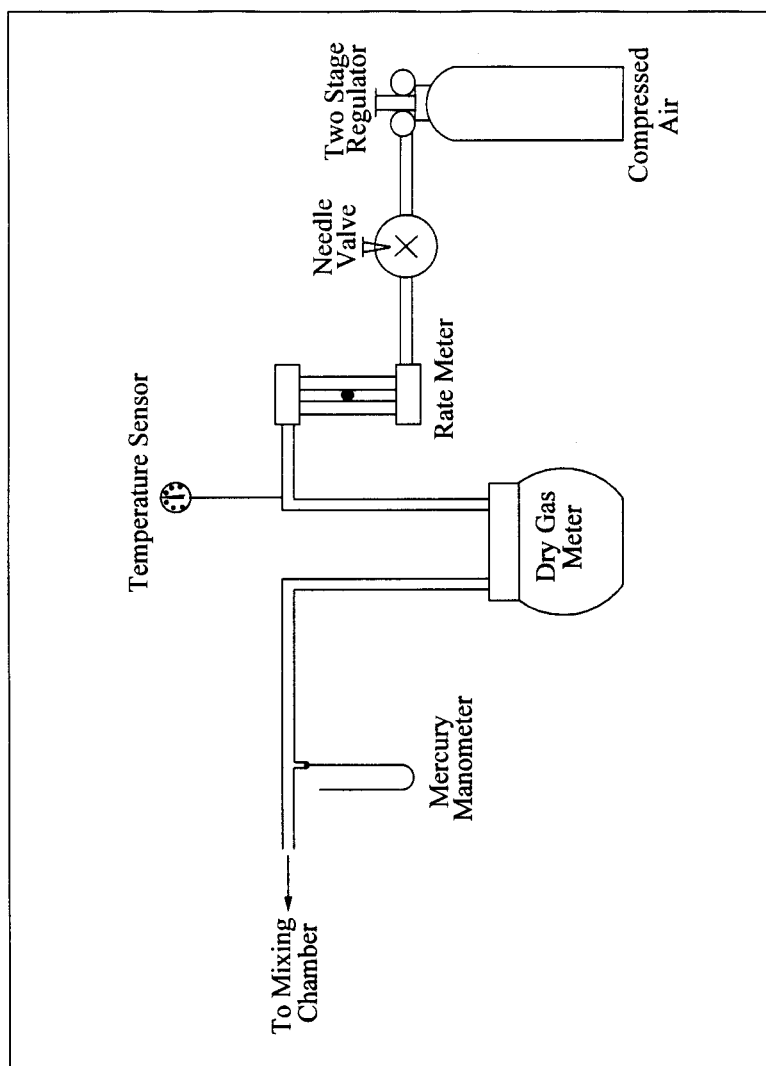


Figure 15A-3. Combustion Air Delivery System.

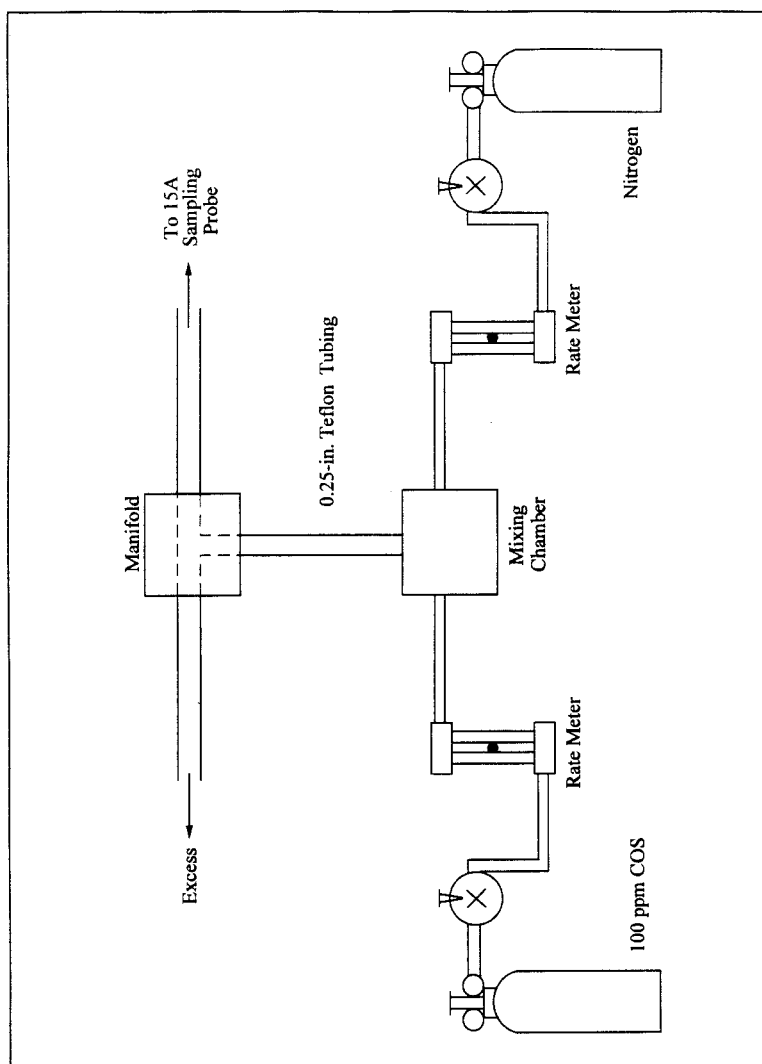


Figure 15A-4. Recovery Gas Generator System.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting part 60, appendix A see the List of CFR Sections Affected, which appears in the Finding Aids section of the printed volume and on GPO Access.

APPENDIX A-6 TO PART 60—TEST  
METHODS 16 THROUGH 18

Method 16—Semicontinuous determination of sulfur emissions from stationary sources

Method 16A—Determination of total reduced sulfur emissions from stationary sources (impinger technique)

Method 16B—Determination of total reduced sulfur emissions from stationary sources

Method 17—Determination of particulate emissions from stationary sources (in-stack filtration method)

Method 18—Measurement of gaseous organic compound emissions by gas chromatography

The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title “Test Methods and Procedures” is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the re-

sults and it is recognized that alternative and equivalent methods exist. Section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and re-testing with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as “subject to the approval of the Administrator” or as “or equivalent.” Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator’s disapproval of the alternative.

METHOD 16—SEMICONTINUOUS DETERMINATION  
OF SULFUR EMISSIONS FROM STATIONARY  
SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 4, Method 15, and Method 16A.

1.0 *Scope and Application*

## 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Dimethyl disulfide [(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub> ] .....	62-49-20	50 ppb.
Dimethyl sulfide [(CH <sub>3</sub> ) <sub>2</sub> S] .....	75-18-3	50 ppb.
Hydrogen sulfide [H <sub>2</sub> S] .....	7783-06-4	50 ppb.
Methyl mercaptan [CH <sub>3</sub> S] .....	74-93-1	50 ppb.

1.2 *Applicability.* This method is applicable for the determination of total reduced sulfur (TRS) compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills and fuel gas combustion devices at petroleum refineries.

NOTE: The method described below uses the principle of gas chromatographic (GC) separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the calibration precision and sample line loss criteria are met.

1.3 *Data Quality Objectives.* Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 *Summary of Method*

2.1 A gas sample is extracted from the emission source and an aliquot is analyzed for hydrogen sulfide (H<sub>2</sub>S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) by GC/FPD. These four compounds are known collectively as TRS.

3.0 *Definitions. [Reserved]*4.0 *Interferences*

4.1 *Moisture.* Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This is prevented by maintaining the probe, filter box, and connections at a temperature of at least 120 °C (248 °F). Moisture is removed in the SO<sub>2</sub> scrubber and heating the sample beyond this point is not necessary when the ambient temperature is above 0 °C (32 °F). Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

4.2 *Carbon Monoxide (CO) and Carbon Dioxide (CO<sub>2</sub>).* CO and CO<sub>2</sub> have a substantial desensitizing effect on the flame photometric detector even after dilution. Acceptable systems must demonstrate that they

have eliminated this interference by some procedure such as eluting these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO<sub>2</sub> in the diluent gas. The CO<sub>2</sub> level should be approximately 10 percent for the case with CO<sub>2</sub> present. The two chromatograms should show agreement within the precision limits of Section 10.2.

4.3 *Particulate Matter.* Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference is eliminated by using the Teflon filter after the probe.

4.4 *Sulfur Dioxide (SO<sub>2</sub>).* Sulfur dioxide is not a specific interferant but may be present in such large amounts that it cannot effectively be separated from the other compounds of interest. The SO<sub>2</sub> scrubber described in Section 6.1.3 will effectively remove SO<sub>2</sub> from the sample.

5.0 *Safety*

5.1 *Disclaimer.* This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 *Hydrogen Sulfide.* A flammable, poisonous gas with the odor of rotten eggs. H<sub>2</sub>S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 *Equipment and Supplies*

6.1. *Sample Collection.* The following items are needed for sample collection.

6.1.1 *Probe.* Teflon or Teflon-lined stainless steel. The probe must be heated to prevent moisture condensation. It must be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas must be heated to prevent moisture condensation. Figure 16-1 illustrates the probe used in lime kilns and other sources where